

PATENT SPECIFICATION

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COMPLETE SPECIFICATION

Improvements in or relating to Removal of Salts from Acetone-Phenol Mixtures

We CALIFORNIA RESEARCH CORPORATION, a Corporation duly organized under the laws of the State of Delaware, United States of America, of 200, Bush Street, San Francisco, 4, California, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The present invention relates to an improvement in the manufacture of phenol.

The newest process for manufacturing phenol from cumene involves, first of all, oxidation of cumene in liquid phase with an oxygen-containing gas, usually air, carried out at a temperature from about 195 to about 240° F. and preferably in the presence of an aqueous alkali to stabilize the hydroperoxide product.

The reaction product mixture obtained in this oxidation represents a solution of cumene hydroperoxide in unreacted cumene together with a small amount of by-products of oxidation, namely dimethyl phenyl carbinol and acetophenone. It is usually preferred to conduct this oxidation in such a manner as to keep the conversion of cumene to cumene hydroperoxide at a level from about 25 to about 35% by weight, based on the initial cumene, since at a higher conversion level the hydroperoxide tends to decompose rapidly, and the yield falls off quite abruptly. In the process step following the oxidation, cumene hydroperoxide present in the oxidation effluent is concentrated, e.g., by fractional distillation at reduced pressure, until its concentration is equal, e.g., to about 90% by weight. In the course of this concentration step, most of the unreacted cumene is separated from the reaction product mixture and recycled to the oxidation stage, while the remaining concentrate of cumene hydroperoxide containing a small quantity of cumene and some dimethyl phenyl carbinol and acetophenone is subjected to a decomposition treatment or cleavage in the presence of an acid catalyst, e.g., sulfuric acid, acetic acid, phosphoric acid, para-toluene sulfonic acid, and

usually in the presence of an inert diluent, at a temperature which may range from about 150 to about 300° F. The effluent from the cleavage treatment contains mainly phenol and acetone and, in addition, a minor quantity of organic by-products such as acetophenone, dimethyl phenyl carbinol, α -methylstyrene, higher phenols (mostly cumyl phenol), acet-aldehyde, some polymers of α -methylstyrene and of acetone, some water, the acid catalyst and organic acidic contaminants formed during the oxidation step and/or under the conditions of the cleavage reaction.

Before attempting to separate phenol and acetone from this complex mixture by a sequence of distillations, it is necessary to neutralize the acid components thereof, and this is effectively accomplished by employing a basic material, e.g., aqueous sodium hydroxide, sodium carbonate, or sodium phenolate. Dependent on whether sulfuric, acetic, phosphoric or para-toluene sulfonic acid has been used to catalyze the cleavage reaction, corresponding sodium salts of these acids may be partly precipitated in the effluent, and can be partly removed by filtration thereof, but even then about 25% of the salt remains in solution in the cleavage product mixture (as indicated by an ash analysis value of 0.17% by weight). While the neutralization of the acid catalyst, such as the neutralization of the most frequently employed sulfuric acid with the aid of aqueous sodium phenolate, eliminates the undesirable acidity, it creates new complications during the subsequent purification and recovery of phenol and acetone by distillation. The inorganic salts, such as sodium sulfate, tend to crystallize, plugging the lines and fouling the equipment (reboilers, etc.), and, as a consequence, the processing of the neutralized cleavage mixture gives rise to the problem of how to remove therefrom these salts. In addition to this problem, two other problems are involved: First, how to prevent corrosion of distillation equipment (stills), caused in part by the decomposition of organic sodium carboxylates during the separation of phenol from

acetone and from the organic by-product impurities; second, how to prevent the presence of hydrocarbon oil (e.g., α -methylstyrene) in the final phenol product so that it would pass the water dilution test required by the current specifications of the industry.

The present invention eliminates the aforementioned difficulties by a very expeditious and inexpensive treatment of the neutralized cleavage mixture containing dissolved therein inorganic and organic salts. We found that on adding water to this neutralized cleavage mixture in an amount sufficient to cause formation of two phases, the upper organic phase will contain phenol, acetone, and water, and the lower aqueous phase having a volume equal to at least 5% of the volume of the organic phase will contain substantially all of the inorganic and organic salts and a minor amount of phenol and acetone. This addition of water and settling of two phases is carried out in the temperature range from about 50 to about 150° F. Most satisfactory results are obtained by adding water to the neutralized cleavage mixture in such quantities that the aqueous phase has a volume equal to from about 8% to about 20% of the volume of the organic phase. Even larger additions of water have been successfully employed resulting the formation of an upper organic phase of phenol, acetone and water and a lower aqueous phase of a volume equal to as much as 50% by volume of the organic phase and containing practically all of the inorganic and organic salts. The removal of salts from the upper phase into the lower phase is entirely unexpected, particularly when it is noted that the upper phase contains not less than 15% by weight of water. The neutralized cleavage mixture already contains some water (from 1 to 3% by weight). Upon the addition of more water to effect the separation of the two phases, the total minimum quantity of water present in both phases is equal to about 45% by weight, based on the phenol component. In addition to the effective removal of salts, it is believed that the presence in the cleavage mixture of hydrocarbons, such as unreacted cumene, α -methylstyrene and its polymers, contributes to a more thorough withdrawal of phenol and acetone into the upper phase, upon addition of water to the neutralized cleavage mixture.

Usually, it is preferred to carry out the cleavage of cumene hydroperoxide in the presence of acetone, which may be conveniently provided by recycling a portion of acetone separated from phenol and dehydrated in the subsequent stages of the process. However, if desired, any other water-miscible and acetone-miscible diluent may be employed in effecting a homogeneous cleavage of cumene hydroperoxide, without any adverse effect upon the success of salt removal from the neutralized cleavage mixture by the addition of water, resulting in the formation of an upper organic

and a lower aqueous phase in accordance with the principle of the present invention. Cumene may also be successfully employed as a diluent, particularly since it is already available in the first oxidation step of the process for manufacturing phenol and may be either added to the cleavage mixture, or all of the cumene or a portion thereof may be permitted to remain in the oxidation product mixture by reducing the thoroughness of the step of concentrating cumene hydroperoxide in the oxidation product mixture.

The removal of salts from the organic phenol-acetone-water phase obtained by the addition of water to the neutralized cleavage mixture is so thorough that the salt content of the organic phase is less than 0.03% by weight (determined by ash analysis). Often the salt content is found to be reduced even further to a figure of the order of 0.01% by weight (as ash). The possibility of obtaining this reduction in the salt content represents a significant improvement over the previously proposed technique of filtration for the removal of salts. As mentioned hereinbefore, filtration, even the most thorough one, leaves as much as 0.17% by weight of salts dissolved in the neutralized cleavage mixture. Furthermore, we pointed out that it does not completely eliminate the dangers of corrosion of the equipment, and, in the subsequent removal of phenol from acetone by distillation, traces of the organic salts, which remain in the filtrate of neutralized cleavage mixture, are likely to decompose into acidic constituents which may promote corrosion.

We said that the addition of water for the purpose of removing (extracting) the salts in accordance with the present invention may be conveniently carried out at a temperature in the range from about 50 to about 150° F. The optimal temperature may vary somewhat depending on the nature of the salt being removed. Thus, when sulfuric acid is employed to split up cumene hydroperoxide and, as a consequence, the salt in the neutralized cleavage mixture mainly consists of Na_2SO_4 , temperatures from 70 to 90° F. are found to be most satisfactory, the lower temperatures in this range requiring employment of less water. For instance, when 25% by weight of water is added to the neutralized cleavage mixture at 75° F., about half of this water goes into the upper organic phase upon phase separation; when the same quantity of water is added at 90° F. about 60% thereof goes into the organic phase. On the other hand, the thoroughness of salt removal, particularly of the organic salts, (as judged from the data of ash analysis) improves at higher temperatures. The amount of water which may be added varies within wide limits, from 15 to 75%, based on the weight of the cleavage reaction mixture, having been successfully employed. This results in the presence of from 2.5 to 56% of water in

the lower phase, based on the volume of the upper organic phase. It will be noted, however, that in employing amounts of water, lower than about 25% by weight, e.g., from 15 to 20% by weight (corresponding to 2.5 to 7% of water in the lower phase based on the volume of the upper organic phase), the temperature should preferably be not less than about 70° F. to avoid the possibility of separation of a solid salt phase.

The exact nature of the phenomena involved in the removal of salts into the lower aqueous phase upon addition of water in accordance with the present invention is not definitely known; it may be that the presence of hydrocarbons in the cleavage mixture, namely α -methylstyrene, its polymers and unreacted cumene, may influence the passage of salts into the lower phase. Whatever be the cause, the addition of water provides a solution to a problem which heretofore constituted a serious drawback for the recovery of phenol. Moreover, the presence of water in the upper phase raises no difficult problem with respect to its subsequent removal to obtain the specification phenol, and, on the contrary, a superior final phenol product is obtained, as rated on the basis of the water dilution test.

For the better understanding of the present invention, reference is made to the accompanying drawing in which Figure 1 diagrammatically represents the general operating features of our method of salt removal (extraction) as applied to a neutralized cleavage mixture produced by heating cumene hydroperoxide with sulfuric acid.

In Figure 1, the reaction mixture leaving the cleavage stage enters a line 1 to be joined by the solution of a neutralizing agent, e.g., 25% solution of sodium phenolate, arriving through a line 2. The mixture enters a mixer 3 and the acid components become thoroughly neutralized, whereupon the neutralized mixture enters a line 4. A stream of water at a suitable temperature arrives through line 5 and joins the neutralized mixture in line 4, whereupon the combined streams enter a mixer 6. After passing through this second mixer, the liquid phenol-acetone-water mixture enters a settler 8, where two phases separate, the lower aqueous phase being recycled through a line 11 to the fresh-water line 5. Upon continued operation (recycling), the concentration of salts in the lower aqueous phase, formed in the settler 8, continually increases, and therefore, a bleed-off line 12 is provided to remove a portion of this lower aqueous phase either to be discarded to the sewer or to recover therefrom minor amounts of phenol and acetone. The upper organic phase containing phenol, acetone and water is sent through line 13 for further processing (separation of phenol from acetone, dehydration and purification of each of them, etc.)

Figure 2 of the same drawing represents a

flow diagram of a particular variant of the method of our invention for salt removal from the reaction mixture resulting after cleavage of cumene hydroperoxide for the purpose of obtaining phenol and acetone. In Figure 2 the cleavage mixture containing phenol, acetone and other organic by-products of the oxidation and cleavage reactions as well as the acid catalyst and some water, passes through line 20 into mixer 21. It is neutralized with the aid of an aqueous solution of an appropriate basic material such as sodium phenolate, carried in line 22. The neutralization is completed in mixer 21 and the neutralized mixture passes through line 23 into mixer 24. Water is introduced into mixer 24 through valve-controlled start-up line 25. From mixer 24, the liquid mixture passes through line 26 into settler 27. Two phases separate in this settler. The lower aqueous phase is recycled through lines 30, 25 and 23 into mixer 24, and the organic upper phase is sent through lines 31 and 32 to a second settler 33, which may be named "organic phase washer". A portion of the aqueous phase from settler 27 is bled off through line 30 and passes through line 34 to distillation column 35 where traces of phenol and acetone are stripped therefrom with the aid of steam. The overhead containing traces of phenol and acetone passes through line 36 to be condensed in condenser 37, whence it flows into a receiver 40. The bottoms from the distillation column 35 represent an essentially phenol-free water solution of the bulk of inorganic and organic salts and are withdrawn through line 41 to a reject pond or may be sent for an additional processing to recover traces of phenol therefrom. The condensed aqueous liquid in receiver 40 is pumped through line 42 to a water storage vessel 43 where it is combined with aqueous phenol produced during the eventual separation of the components of the salt-free mixture coming out from settler 33 through line 44, and with whatever amount of make-up water may be necessary. From water storage vessel 43, water is pumped by pump 45 through lines 46 and 32 into settler 33 where two phases, an upper organic phase and a lower aqueous phase, are formed. The aqueous phase is recirculated through lines 47 and 32 to insure the desired thoroughness of the salt removal until the ultimate salt content of the upper organic phase is not higher than 0.03% by weight (based on the initial cleavage product mixture and determined by ash analysis). This substantially salt-free phenol-acetone-water upper phase is withdrawn through line 44 to be further processed, namely, to separate phenol and acetone from each other and from other impurities. This may be done, e.g., by a succession of fractional distillations, in which, first, an acetone-rich fraction is recovered overhead and a phenol-rich fraction containing

water and minor amounts of organic impurities is recovered as bottoms; thereupon the acetone overhead is successively distilled to remove acetaldehyde and to separate substantially pure acetone from water, phenol and other admix-
 5 tures while the phenol-rich bottoms fraction is also treated in a succession of distillations to separate substantially pure phenol from a frac-
 10 tion containing water and organic impurities, such as α -methylstyrene and unreacted cumene. Upon settling of this latter fraction or of the bottoms from the distillation of pure acetone, two phases are formed: A water phase and an oil phase containing the organic impurities.
 15 These two phases may be readily separated from each other, e.g., by decantation, and the water phase may be rejected to sewer. How-
 20 ever, since this water still contains traces of phenol, it is recycled, either entirely or in part, to be combined with the make-up water being added to the neutralized cleavage mixture. A
 portion of the lower aqueous phase from settler 33 is diverted by way of line 47 into
 25 line 25 and line 23 where it will be combined with the incoming neutralized cleavage mixture about to enter the salt removal stage of the process.

The removal of inorganic and organic salts
 30 in accordance with our invention may be also achieved by using more water in forming aqueous dilutions of basic materials, such as sodium hydroxide, sodium phenolate or sodium carbonate, to neutralize the acidity in the cleav-
 35 age product mixture. Thus, in lieu of 25% by weight of sodium phenolate, a dilution of approximately 5.0% of sodium phenolate could be used. Instead of introducing the water at a point subsequent to the introduction of
 40 sodium phenolate or a similar neutralizing agent, the two streams may be combined, eliminating thereby the requirement for additional mixing equipment such as mixer 6 in Fig. 1 and mixer 24 in Fig. 2. The make-up
 45 water and the aqueous phenol recycle may likewise be combined with the stream of aqueous neutralizing agent.

The thoroughness of the salt removal obtained in accordance with the method of our
 50 invention is amply illustrated by the following example in which a typical cleavage mixture was employed. This mixture was neutralized on leaving the cleavage vessels with a solution (37%) of sodium phenolate. It contained:—

	Per cent by weight
55 Phenol - - - - -	40.3
Acetone - - - - -	45.0
Hydrocarbons - - - - -	4.6
60 Water - - - - -	3.6
Organic impurity (acetophenone, etc.) - - - - -	5.4
Sodium sulfate - - - - -	0.9
Unidentified - - - - -	0.2
65 Total	100.0%

Water was added to this cleavage mixture in an amount equal to 26.6% by weight thereof, and two phases separated, the temperature being in the region of 90° F. The upper organic phase took up 12% by weight of the
 70 added water, while the lower phase was found to have a volume equal to about 14.5% of the volume of the organic phase and, upon analysis, showed the following composition:—

78.9% by weight of Water	75
5.5% by weight of Salt	
1.2% by weight of Phenol	
14.4% by weight of Acetone	

100.0% Total

The salt content in the organic phase deter-
 80 mined by the ash analysis of phenol was a mere 0.03% by weight as compared to the value of 0.16% by weight obtained from a similar cleavage mixture after it was filtered to effect removal. 85

What we claim is:—

1. A process for the production of phenol and acetone from cumene hydroperoxide, in which cumene hydroperoxide is decomposed in the presence of catalytic amounts of an acid, 90 the acid and acidic organic impurities in the decomposition mixture are neutralized and the salts produced by this neutralization are removed, wherein water is added to the decom-
 position mixture in a proportion sufficient to 95 form, upon neutralization and settling, an organic upper phase containing substantially all of the phenol and acetone and some water, and an aqueous lower phase having a volume equal to at least 5% of the volume of the organic 100 phase and containing in solution substantially all of the salts formed by this neutralization, and the said organic upper phase is separated from the aqueous lower phase.

2. A process as claimed in claim 1, wherein 105 the water is added prior to the neutralization of decomposition mixture.

3. A process as claimed in claim 1, wherein the water is added after the neutralization of the decomposition mixture. 110

4. A process as claimed in any of claims 1 to 3, wherein cumene hydroperoxide is decomposed in the presence of an inert, water-miscible and acetone-miscible diluent.

5. A process as defined in claim 4, wherein 115 the inert diluent is acetone.

6. A process as claimed in any of claims 1 to 5, wherein the addition of water and the settling of the phases is carried out at a tempera-
 120 ture of from about 50° F. to about 150° F.

7. A process as claimed in any of claims 1 to 7, wherein the water is added in such a pro-
 125 portion that the resulting aqueous lower phase has a volume of from at least 5% to about 50% of the volume of the organic phase.

8. A process as claimed in claim 7, wherein the water is added in such a proportion that the resulting lower aqueous phase has a volume of from about 8% to about 20% of the volume of the organic phase. 130

9. A process as claimed in any of claims 1 to 8, wherein cumene hydroperoxide is decomposed at a temperature from about 150° F. to about 300° F.

5 10. A process as claimed in any of claims 1 to 9, wherein the neutralized decomposition mixture is allowed to settle at a temperature of from about 70° F. to about 90° F.

10 11. A process as claimed in any of claims 1 to 10, wherein the acid is an inorganic acid.

12. A process as claimed in claim 11, wherein the acid is sulfuric acid.

15 13. A process as claimed in any of claims 1 to 12, wherein the decomposition mixture is neutralized by an aqueous solution of sodium phenolate.

20 14. A process as claimed in any of claims 1 to 12, wherein the cumene hydroperoxide is obtained by oxidizing liquid-phase cumene with an oxygen-containing gas in the presence of an aqueous alkali to form an oxidation product mixture comprising cumene hydroperoxide and unreacted cumene and separating substantially all of the unreacted cumene from the cumene hydroperoxide.

25 15. A process as claimed in claim 14, wherein cumene is oxidized with air.

30 16. A process as claimed in any of claims 1 to 13, wherein the phenol and acetone are recovered from the organic phase by fractional distillation.

35 17. A process as claimed in claim 16, wherein the upper phase is fractionally distilled to separate an overhead fraction comprising acetone and a bottoms fraction comprising

phenol, water and minor amounts or organic impurities, the bottoms fraction is distilled to separate phenol from a fraction comprising water and substantially all of the organic impurities, and this latter fraction is allowed to settle to separate a water phase from an oil phase containing the organic impurities. 40

18. A process as claimed in claim 17, wherein at least a portion of said water phase is recycled to the decomposition mixture. 45

19. A process as claimed in claim 17 or 18, wherein the overhead fraction is distilled to separate acetone from a fraction comprising water and substantially all the organic impurities. 50

20. A process for the production of phenol and acetone from cumene hydroperoxide substantially as hereinbefore described with reference to the specific example and the accompanying drawings. 55

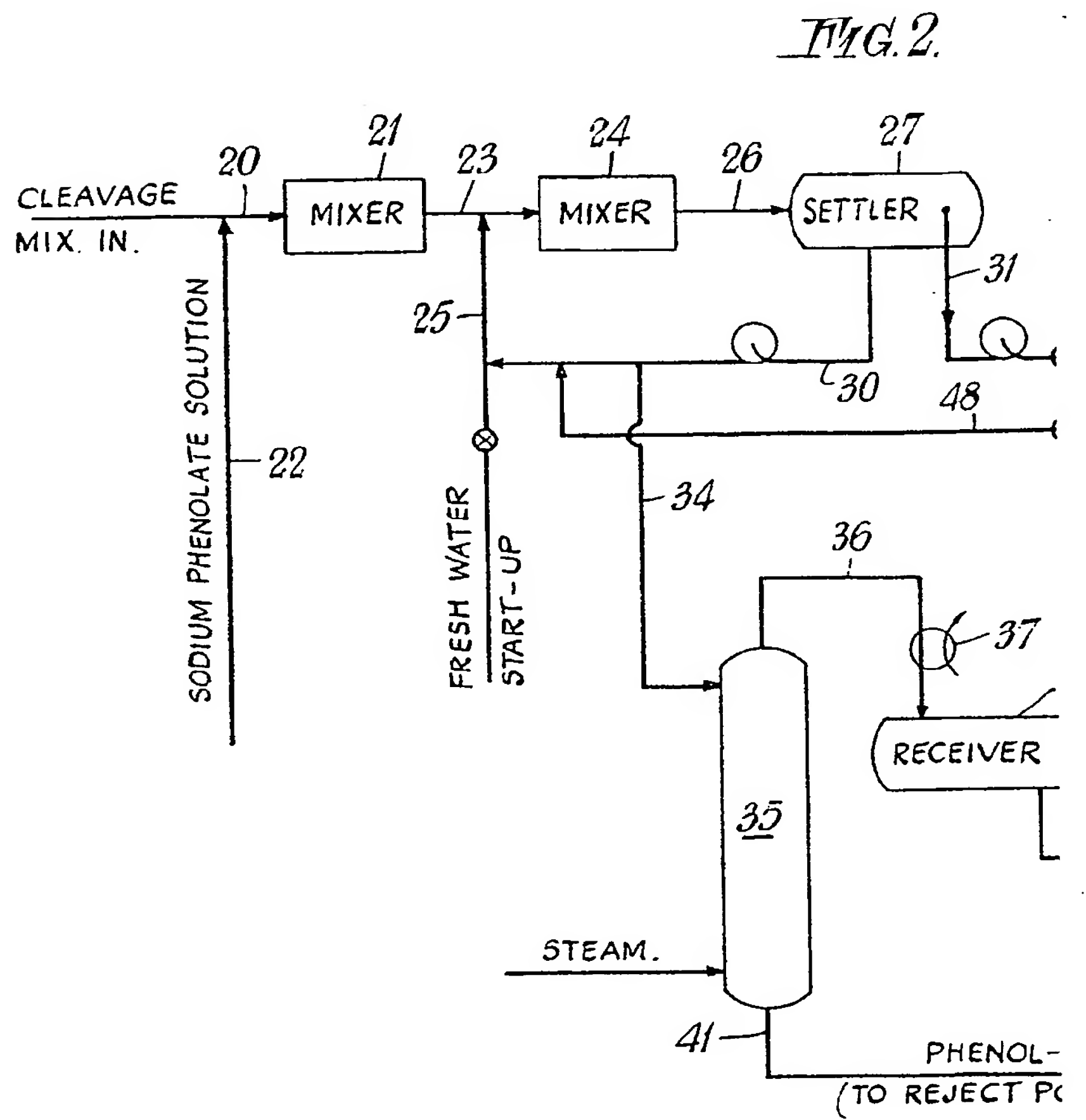
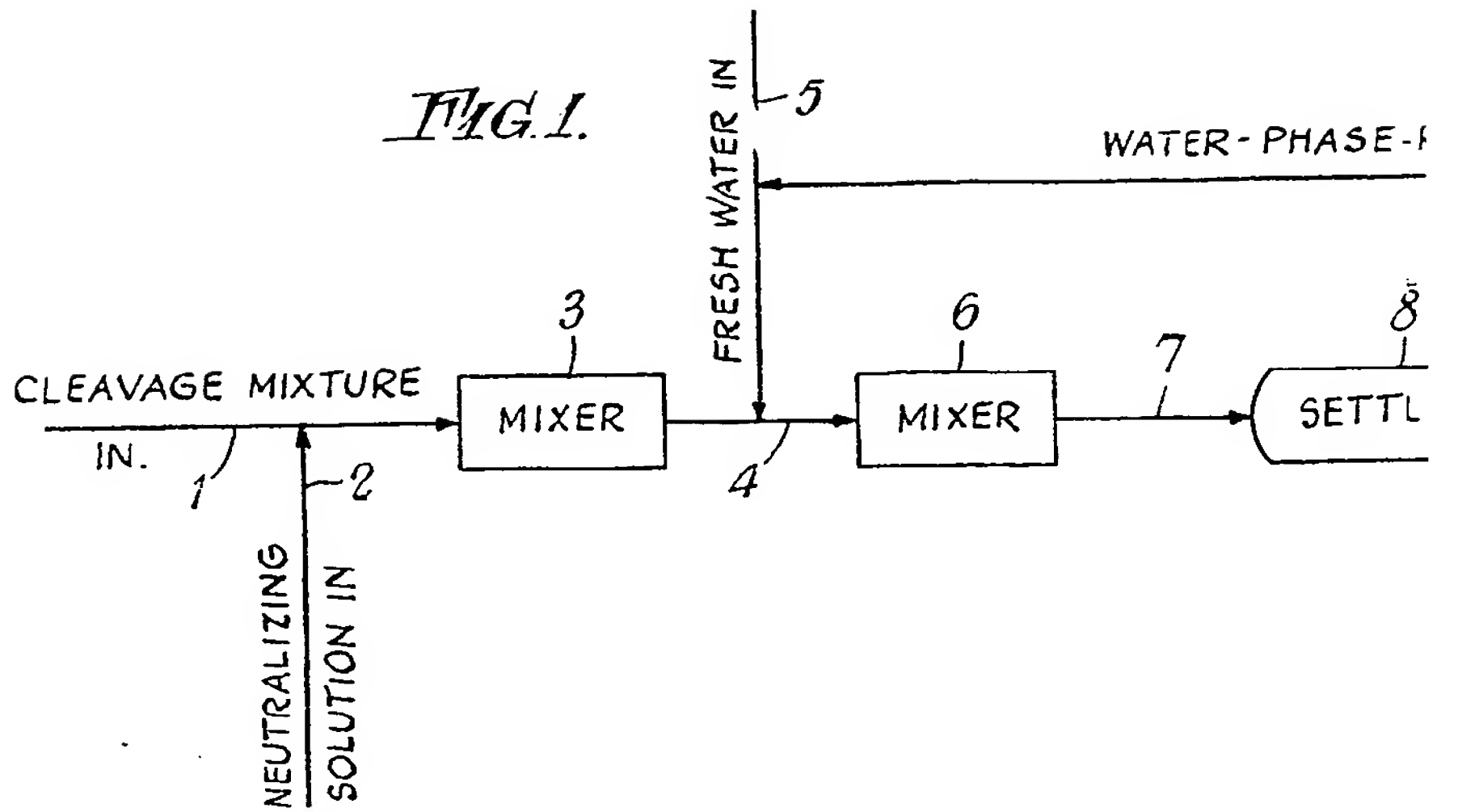
21. A process for the production of phenol and acetone from cumene substantially as hereinbefore described with reference to the specific example and the accompanying drawings. 60

22. Phenol and acetone, where prepared by the process claimed in any of claims 1 to 21.

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Reference has been directed in pursuance of Section 9, Subsection (1) of the Patents Act, 1949 to Patents Nos. 684,039, 629,429 and 626,095.

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743.004 COMPLETE SPECIFICATION

1 SHEET

This drawing is a reproduction of the Original on a reduced scale.

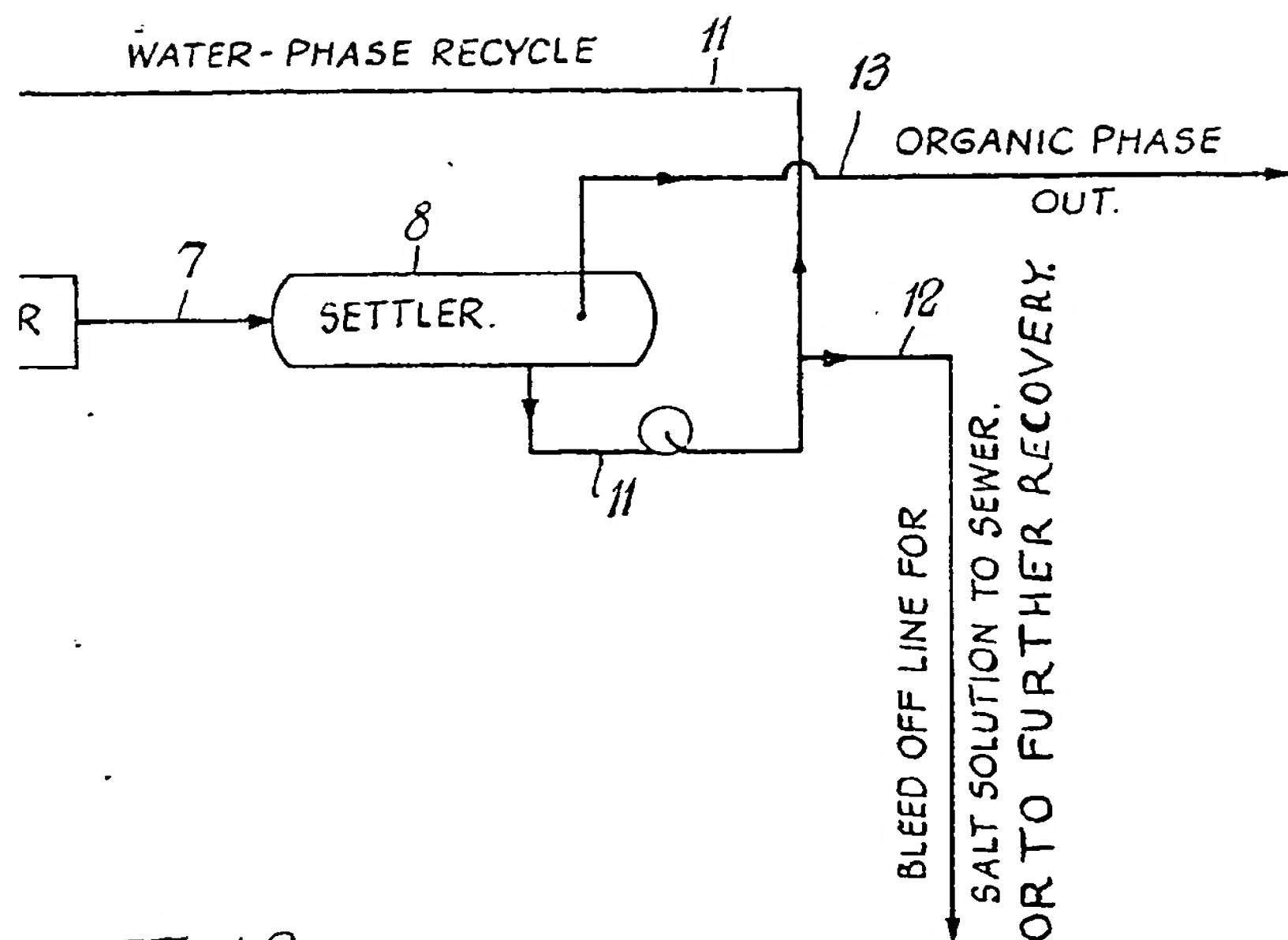


FIG. 2.

